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HEAVY METALS IN FISH AND INVERTEBRATES FROM THE GULF OF PARIA, VENEZUELA

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Key words: heavy metals, bioaccumulation, invertebrates, contamination, fish

ABSTRACT

The concentration of Hg, Cu, Cd, Cr and Ni was estimated in fish and invertebrates captured in the Gulf of Paria coastal zone, Venezuela. The results show that invertebrates have a higher bioaccumulation of metals in relation to fish, particularly *C. virginica* that had the highest concentrations of Hg, Cu and Cd and the snail *A. deflorata* with the highest values of Cr, Ni and Pb. In relation to fishes, *C. spixii* (catfish) presented the highest values of all metals tested. The metals tested in the species do not exceed the maximum permissible values indicated by the WHO for human consumption. However, heavy metals are present in the Gulf of Paria.

Palabras clave: metales pesados, bioacumulación, invertebrados, contaminación, peces

RESUMEN

En el presente trabajo se evaluó la concentración de Hg, Cu, Cd, Cr, Ni en peces e invertebrados capturados en la zona costera del Golfo de Paria, Venezuela. Los resultados muestran que los invertebrados tienen mayor bioacumulación de metales en relación a peces, particularmente *C. virginica* presentó la mayor concentración de Hg, Cu y Cd y el caracol *A. deflorata* que presentó las mayores concentraciones de Cr, Ni y Pb. En peces el bagre *C. spixii* presentó los más elevados valores de los metales analizados. Los metales evaluados en las especies no superen los valores máximos permisibles señalados por la Organización Mundial de la Salud para consumo humano, sin embargo se determina la presencia de los metales en el Golfo de Paria.

INTRODUCTION

The use of organisms to evaluate heavy metals in environmental conditions is often a good indicator of the health of ecosystems, especially when it comes to persistent pollutants such as heavy metals (Islam and Tanaka 2004, Pascual and Avollo 2005). Most organisms can take trace metals from the sediment and the water column and concentrate them in their tissues. In fact, a wide variety of species can be used as biomonitors to evaluate ecosystems affected by trace metals (Rojas *et al*. 2009, Lemus *et al.* 2010).

Moreover, the USA Federal Drug Administration (2001) states that authorities responsible for health services must carry out frequent monitoring on the quality of fish and shellfish intended for human consumption.

Some heavy metals (Hg, Cd, Pb) are regarded as the most dangerous pollutants now existing. Others such as Cu and Zn, although essential for living organisms, are also toxic when certain threshold concentrations are exceeded.

When trace metals are dumped into the aquatic environment they may be biologically fixed into marine organisms from the surrounding water or by ingestion of food and sediment particles. Invertebrates and fish are specific indicators of different environmental compartments in relation to their habitat and trophic chain position, and they exhibit different rates of bioaccumulation with respect to different heavy metals.

The eastern area of Venezuela does not have extensive industrial development, particularly the coast of the Sucre State; however there are port activities in Güiria, together with oil exploitation sites and refining plants in the southern part of the Gulf. Directed toward this and other parts of the eastern region, important projects are being put forward to exploit natural gas reserves and further condensed hydrocarbon products in offshore oil deposits. These reserves are located to the north of Paria Peninsula, where the basic resource extraction activities will be carried out. This project covers an area extending to the south-east of the peninsula.

Recently, no research has been done on metal monitoring in the Gulf of Paria, except for metal evaluation in *Perna viridis, Crassostrea virginica* and *Crassostrea rizophorae* in 1999 at six locations of the gulf and three locations on the coast of Trinidad (Rojas *et al*. 2002).

In this research, an analysis of the metals Cu, Cd, Cr, Ni, Pb, and Hg is performed in fish and invertebrates from locations of the northern coast of the Gulf of Paria.

MATERIALS AND METHODS

Fish and invertebrate specimens were collected in four sampling areas along the northern coast of the Gulf of Paria (**Fig. 1**). The six most abundant species, *Stillifer rastrifer, Cathorops spixii, Pellona harroweri, Selene vomer, Lutjanus synagris, Diapterus rhombeus* and the white shrimp *Litopenaus schmitti*, were collected by traditional fishing methods in Los Trancotes, Soro and Macuro. In addition, *Crassostrea virginica,*

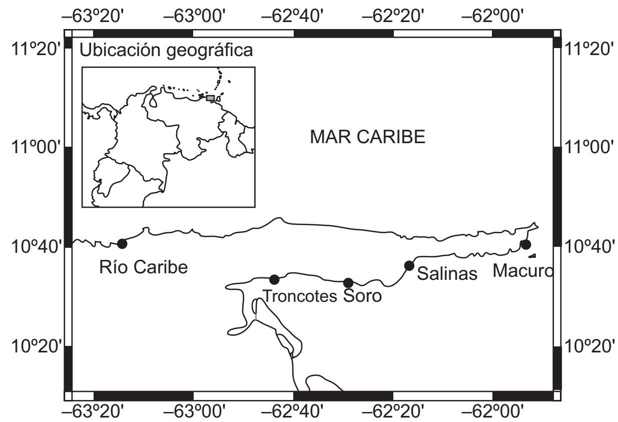

Fig. 1. Map showing fish and invertebrate collecting areas in the Gulf of Paria

Cyclinella tenuis, and *Asaphys deflorata* were manually collected in Macuro, Soro and Las Salinas.

The specimens were separated by species in labeled PVC bags and taken to Laboratory of the Instituto Oceanográfico de Venezuela (IOV) (for its acronym in Spanish). At the IOV, their morphometric characteristics were recorded, the specimens were dissected and their tissues were prepared for metal analysis.

Both fish and crustaceans and mollusks underwent the extraction of all the soft tissue from six organisms, while fish underwent the extraction of all the visceral mass before processing. All organisms were washed with distilled water and an EDTA solution at 1 % m/v in order to eliminate metals adsorbed onto the surface, and then they were dried in a stove at 60 ºC until reaching a constant weight. The tissues used to determine the quantity of mercury and the other metals were dried separately.

To determine Cu, Cd, Cr, Ni, and Pb, the samples, once dried, underwent a pre-digestion with 8 mL of concentrated nitric acid (analytic degree, Merk), during the night at room temperature with adequate controls. A digestion was subsequently carried out for six hours at 60 ºC, and after the sample cooled off, about 6 mL of deionized water was added and the filtering of the sample was performed up to a total volume of 25 mL in flasks until the moment of analysis. Results were expressed in µg/g dry weight (DW). The method used to determine metals was validated with certified reference materials (DORM- 2 and LUTS-1). Standards for all metals were analyzed simultaneously with the experimental samples

To determine Hg the samples were weighed in plastic containers and dried until reaching a constant weight at 60 ºC. Then nitric acid was added in a 1 g/3 mg ratio and the sample was left to pre-digest overnight.

Digestion was completed at a 60 ºC temperature for six more hours and finally sulfuric and hydrochloric acids were added keeping an 8:2:1 v/v ratio between all three acids (Rojas *et al.* 2002).

The determination of Hg by cold vapor was performed chemically reducing mercury to the atomic state with $NaBH_4$ at 3 % in NaOH at 1 % in a tight reaction container. The detection limit is approximately 0.000460 µg/L where a 1 % of absorbance change represents 4.68 ng. The wavelength used was 253.6 nm and the calibration curve was 100, 200, and 500 ng following Perkin Elmer´s instructions (1972). The validation of the method was performed as mentioned in the previous paragraph for the other metals. Results were expressed in µg/g of dry weight.

RESULTS AND DISCUSSION

Heavy metal research in fish and invertebrates from the Gulf of Paria represents a contribution to the understanding of metal bioaccumulation in six fish species and five invertebrate species, since until now no research has been done on metal evaluation in several species of this gulf. However, sufficient records of heavy metal levels in sediments and waters can be found (Márquez *et al.* 2000, Rojas *et al.* 2005),

The results obtained in this investigation show that the study area has no evidence of significant levels of mercury for the analyzed species. Mercury levels for the six species ranged from 0.005 ± 0.005 to 0.016 ±0.008 µg/g, with the highest concentration being found in the catfish *C. spixii* in Soro and Trancotes locations, and *S. vomer* from Soro. Mercury concentrations in the three bivalve species evaluated in the Gulf of Paria were higher than those detected for fish, with values between 0.026 ± 0.016 and 0.148 ± 0.107 µg/g, the latter being the average value of the oyster *C. virginica* from Macuro location (**Table I**).

From the results of this research, none of the species under study exceeded the maximum limit allowable indicated by the World Health Organization (1976), but it is important to point out that *C. virginica* showed the highest concentration founded (0.05 ± 0.01) in the location of Chacachacare on the northern coast of Trinidad (Rojas *et al.* 2002). These results show that there has been an increase in the concentration of this metal in *C. virginia*.

Although no anthropic sources of mercury are known in the zone, it is possible that the mercury in the oyster *C. virginica* comes from matter in suspension arriving from the Orinoco delta. This is a site in which an elevated concentration of this metal is found, as a result of gold mining activities (Rojas *et al.* 2005, Pirrone *et al.* 2010). On the other hand, the yearly concentration of Hg in the bivalve *P. viridis* from the north coast of the Peninsula of Paria was 0.45 µg/g of dry mass, which indicates the presence of this metal in this zone (Rojas *et al*. 2009).

The copper content in fish from the locations of the Gulf of Paria ranged from 0.62 ± 0.14 µg/g for *L. synagris* of Macuro location to 1.39 ± 0.22 for the catfish *C. spixii* of Los Trancotes. Fish of this same species from Las Salinas showed a similar value (**Table II**).

TABLE I. MERCURY CONCENTRATIONS (µg/g dry weight) IN FISH AND INVERTEBRATES FROM THE NORTHERN COAST OF THE GULF OF PARIA

	Location	Total Length (cm)	Average (µg/g)	Range
Fish				
Stellifer rastrifer	Trancotes	7.33 ± 0.74	0.010 ± 0.008	0.001 – 0.023
Cathorops spixii	Trancotes	8.21 ± 0.40	0.015 ± 0.010	0.000 – 0.028
Pellona harroweri	Soro	8.75 ± 0.39	0.007 ± 0.003	0.001 – 0.009
Cathorops spixii	Soro	8.76 ± 0.89	0.012 ± 0.006	0.003 – 0.020
Selene comer	Soro	6.05 ± 1.19	0.016 ± 0.008	0.005 – 0.030
Lutjanus synagris	Macuro	6.88 ± 0.96	0.005 ± 0.005	0.000 – 0.013
Diapterus rhombeus	Macuro	6.65 ± 0.75	0.006 ± 0.010	0.000 – 0.028
Invertebrates				
Litopenaeus schmitti	Trancotes	10.30 ± 0.36	0.005 ± 0.005	0.000 – 0.014
Cyclinella tenuis	Soro	2.45 ± 0.12	0.049 ± 0.030	0.099 – 0.015
Asaphys deflorata	Salinas	4.80 ± 0.32	0.026 ± 0.016	0.002 – 0.047
Litopenaeus schmitti	Salinas	11.71 ± 0.75	0.011 ± 0.008	0.004 – 0.027
Crassostrea virginica	Macuro	5.70 ± 0.45	0.148 ± 0.107	0.031 – 0.308

Values are showed as mean and standard deviation. Metal concentration are displayed as mean and range

TABLE II. HEAVY METAL CONCENTRATIONS (μg g^{-1} dry weight) IN FISH AND INVERTEBRATES FROM THE NORTHERN COAST OF THE GULF OF PARIA

Species	Location	Total length (cm)	Weight (g)	Cu (μg/g)	Cd (μg/g)	Cr (μg/g)	Ni (μg/g)	Pb (μg/g)
Fish								
Stillifer rastrifer	1	6.64 ± 2.22	7.65 ± 2.22	1.26 ± 0.71	2.71 ± 1.47	0.14 ± 0.12	0.20 ± 0.29	0.04 ± 0.09
				0.57 – 2.64	1.33 – 5.00	0.04 – 0.36	0.00 – 0.69	0.00 – 0.21
Cathorops spixii	1	8.53 ± 0.73	9.25 ± 1.74	1.39 ± 0.22	6.57 ± 6.38	0.25 ± 0.19	0.18 ± 0.17	0.13 ± 0.11
				1.11 – 1.68	1.76 –18.26	0.08 – 0.61	0.00 – 0.37	0.00 – 0.27
Pellona harroweri	2	6.20 ± 3.84	8.73 ± 1.75	0.75 ± 0.10	1.29 ± 0.77	0.24 ± 0.25	0.08 ± 0.20	0.03 ± 0.07
				0.60 – 0.85	0.16 – 2.30	0.00 – 0.70	0.00 – 0.50	0.00 – 0.18
Cathorops spixii	2	6.26 ± 3.85	7.88 ± 3.03	1.35 ± 0.38	3.13 ± 1.76	0.63 ± 0.74	0.12 ± 0.23	0.08 ± 0.20
				0.88 – 1.99	1.02 – 6.08	0.08 – 1.93	0.00 – 0.58	0.00 – 0.50
Selene vomer	2	6.86 ± 3.84	9.95 ± 5.04	0.68 ± 0.21	3.02 ± 1.56	0.18 ± 0.06	0.01 ± 0.02	–
				0.47 – 1.04	1.30 – 4.72	0.12 – 0.25	0.00 – 0.05	–
Lutjanus sinagris	4	3.43 ± 3.03	10.17 ± 3.97	0.62 ± 0.14	2.00 ± 2.41	0.15 ± 0.11	0.01 ± 0.02	–
				0.41 – 0.79	0.03 – 6.52	0.04 – 0.36	0.00 – 0.04	–
Diapterus rhombeus	4	7.20 ± 1.30	5.48 ± 2.73	0.65 ± 0.36	4.71 ± 2.30	0.20 ± 0.12	–	0.01 ± 0.02
				0.20 – 1.11	1.19 – 8.38	0.04 – 0.35	–	0.00 – 0.02
Invertebrates								
Litopenaeus schmitti	4	6.95 ± 1.30	28.03 ± 6.92	6.9 ± 3.80	5.47 ± 2.83	0.47 ± 0.38	0.44 ± 0.61	0.07 ± 0.09
				3.22 – 10.76	2.01 –10.58	0.02 – 1.21	0.00 – 1.35	– 0.22
Litopenaeus schmitti	4	11.72 ± 4.18	10.78 ± 1.98	16.16 ± 3.80	5.60 ± 5.19	0.10 ± 0.08	0.07 ± 0.13	–
				9.94 – 21.19	0.75 –14.95	0.02 – 0.23	0.00 – 0.32	–
Asaphys deflorata	3	5.607 ± 0.303	19.350 ± 2.619	4.87 ± 0.68	3.28 ± 2.18	1.36 ± 0.35	1.92 ± 0.58	1.89 ± 0.79
				3.92 – 5.91	0.61 – 5.60	0.86 – 1.75	1.00 – 2.52	0.55 – 2.69
Cyclinella tenuis	2	3.01 ± 0.311	7.30 ± 2.22	12.71 ± 20.76	3.94 ± 2.09	0.79 ± 1.60	–	1.35 ± 1.93
				1.83 – 55.00	1.25 – 6.75	0.00 – 4.00	–	0 – 4.25
Crassostrea virginica	4	8.17 ± 1.46	83.97 ± 39.07	45.18 ± 7.46	18.52 ± 3.68	0.19 ± 0.26	0.29 ± 0.28	0.14 ± 0.23
				35.44 – 55.73	22.31 –73.75	0.00 – 0.64	0.00 – 0.61	0 – 0.52

Values are showed as mean and standard deviation. Metal concentration are displayed as mean and range Locations: 1, Trancotes; 2, Soro; 3, Salinas; 4, Macuro

As far as invertebrates are concerned, it was evidenced that copper levels are higher than those detected for fish, with the highest value being for the oyster *C. virginica* from Macuro (**Table II**). This last species was the only one evaluated which exceeded the maximum level allowable. Similar results were obtained by Rojas *et al.* (2002) in five of the ten stations evaluated in the same area.

In fish, the highest Cd concentration was found in the catfish *C. spixii* from Los Trancotes and the seabream *D. rhombeus* from Macuro. The catfish was the only organism exceeding the maximum level allowable and the seabream approaches this limit but the other species do not surpass it.

Cadmium concentrations in invertebrates ranged from 3.94 to 5.47 µg/g except for the oyster *C. virginica* from Macuro, which showed an average value of 18.52 ± 3.69 µg/g (**Table II**). With regard to invertebrates the white shrimp and the oyster exceeded allowable levels. This last value is considerably greater than the values for this same species in 1999, when a maximum concentration of 0.530 ± 0.002 µg/g wet weight was reached.

The highest concentration of chromium in organisms from the Gulf of Paria was detected in the catfish *C. spixii* from the Soro location, with an average value of 0.63 ± 0.74 µg/g, whereas the lowest was found in the guanapo porgy *L. synagris* from Macuro. The levels of this metal in invertebrates remained similar to those in fish; however, the clam *A. deflorata* from Salinas showed an average value of 1.36 ± 0.35 µg/g (**Table II**).

Nickel was not detected in the seabream *D. rhombeus* and the highest levels were found in the catfish *C. spixii* from the two locations evaluated (0.18 ± 0.17 µg/g for los Trancotes and 0.12 ± 0.23 µg/g for Soro) in the Gulf of Paria. Concentrations in invertebrates had the same magnitude as for fish, except the clam *A. deflorata* from Las Salinas (1.92 ± 0.58 µg/g) (See **Table II**).

Lead was not detected neither in the guanapo porgy *L. synagris* nor *S. vomer*, and the greatest concentration was present in the catfish *C. spixii* from Los Trancotes and Soro locations, with concentrations of 0.13 ± 0.11 and 0.08 ± 0.20 µg/g, respectively (**Table II**). The metal was not present in the white shrimp *L. schmitti*, and the greatest concentrations were detected in clams *C. tenuis* and *A. deflorata* with values of 1.35 ± 1.93 and 1.84 ± 0.79 µg/g, respectively.

These results show a differential incorporation of the evaluated metals, with a greater tendency towards increase of bioaccumulation in invertebrates, particularly *C. virginica* and *A. deflorata*. The former had the biggest capacity for accumulating Hg, Cu and Cd, meanwhile the second had it for Cr, Ni and Pb. Obviously bioaccumulation is a complex process that is not only determined by the routes of exposure, either through diet or directly through the gills and contact between the water column, but also by geochemical effects on the metal availability.

The regulation of metals by some species is not less important. In such a way, many organisms have a higher incorporation rate of purification or vice versa, which determines the total load of metal in the soft tissue of an organism and therefore bioaccumulation of it, without implying a toxic effect of the element (Louma and Raimbow 2005).

Fish were juveniles in general and these organisms are highly mobile so this would explain a lower bioaccumulation of metals, but the catfish *C. spixii* was the exception and this can be accounted to the feeding habits of the species. This species is characterized by omnivorous feeding, where much of their food is made up of copepods and other organisms living in the benthos, which is why much of the ingested food consists on sediment, particularly mud or very fine sediment and thus can ingest existing metals (Villares *et al.* 2005).

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